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INVESTIGATION OF METHODS TO ELIMINATE VOLTAGE DELAY IN LI/SOCL --ETC(U)

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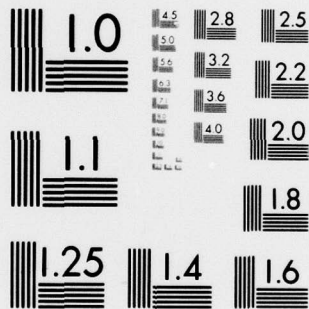


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INVESTIGATION OF METHODS TO
ELIMINATE VOLTAGE DELAY IN
Li/SOCl₂ CELLS

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November 1979

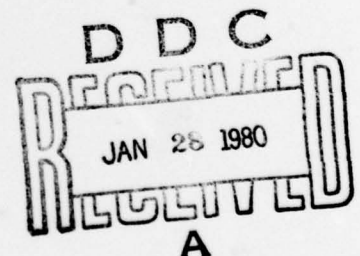
Quarterly Technical Report for Period 19 December 1978 - 19 March 1979

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QUARTERLY TECHNICAL REPORT
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CONTRACT NO. DAAB07-78-C-0558

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ABSTRACT - Continued

resistivity of LiCl layers was found to be lower. For higher A/V ratios, the film was thicker. The salt $\text{Li}^{+}_{10}\text{B}^{+}_{10}\text{Cl}^{-}_{10}$ was found to have lower thermal stability than anticipated, and underwent partial decomposition when heated above 200°C to remove tetrahydrofuran following purification by crystallization from this solvent.

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FOREWORD

Some of the results described in this report were not obtained specifically for this contract, but have been included because of their relevance to the particular subject.

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1. INTRODUCTION

This report is part of a continuing fundamental study of the formation and growth of lithium chloride films on lithium metal exposed to thionyl chloride based electrolytes. Passivation of the lithium electrode resulting from excessive growth of the film has been shown to be responsible for voltage delay in lithium/thionyl chloride cells.^(1,2)

Recent theories have proposed that the lithium chloride film consists of two layers. The inner layer or solid electrolyte interphase (SEI) is thin, compact and completely covers the surface of the lithium. The other is thicker, more porous, and consists of corrosion products outside of the inner layer.⁽³⁾ The outer layer rather than the inner layer is believed to be responsible for the voltage delay.⁽⁴⁾ Using constant current pulses the properties of the inner of the two films can be examined.^(4,5,6)

Examination of the inner film by these techniques during the previous quarter revealed that storage temperature did not appear to affect the growth rate or the reaction resistance of the inner film when these were measured at room temperature.⁽⁷⁾ Since the voltage delay is made worse by storage at elevated temperature, the connection between the delay and the electrical properties of the inner film was not clear. Therefore, these properties were studied for this report by measuring them at the temperatures used to store the samples.

The ratio of the area of lithium surface to the solvent volume has been shown to affect the stability of lithium in organic solvents.^(8,9) The effect is apparently the result of reduction products which aggravate decomposition of the solvent. Although reduction products are not expected to catalyze decomposition of SOCl_2 in Li/SOCl_2 cells, these products may affect the rate or extent of growth of the LiCl layers on lithium in SOCl_2 based electrolytes. Variation in the growth rate and the thickness of the inner film has occurred which cannot be explained on the basis of experimental uncertainty. It had not previously been determined whether any correlation existed between this variation and the ratio of exposed lithium surface to solvent volume.

On the basis of information concerning the high degree of thermal stability of the cesium salts,⁽¹⁰⁾ the lithium salts of $\text{B}_{10}\text{Cl}_{10}^{2-}$ and $\text{B}_{12}\text{Cl}_{12}^{2-}$ were assumed to have similar kinetic stability at elevated temperature. The final step in the preparation of $\text{Li}_2\text{B}_{10}\text{Cl}_{12}$ is purification by crystallization from tetrahydrofuran-water followed by heating under vacuum for several days, which is required to remove the ether. Previously, the temperature chosen for this final process was 160°C , as

dictated by the limit of the available apparatus. A new all glass vacuum line capable of handling sample sizes in the appropriate range became available to heat $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ and $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$ solvates beyond this without risking contamination. It was decided to attempt heating of these salts beyond 200°C in order to expedite the removal of solvents from the purified or crystallized product, but the affect of this process on the structure of the salts was not thoroughly understood.

2. EXPERIMENTAL

2.1 PREPARATION OF $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ AND $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$

The preparation and purification of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ was similar to the complete description given in the first quarterly report⁽⁷⁾ except that following the crystallization of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$, removal of tetrahydrofuran and water were attempted in all glass vacuum apparatus in which the salt was heated in vacuo between 200-300°C for several days.

The preparation of $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$ began with the synthesis of the anion $\text{B}_{12}\text{H}_{12}^{2-}$ from decaborane (Callery Chemical) and triethylamine borane (Aldrich Chemical) according to the method of Miller and Muettterties.⁽¹¹⁾ A solution was prepared by adding a solution of 30 g of $\text{B}_{10}\text{H}_{14}$ (0.246 m) to 79 ml (62.5 g or 0.54 m) of triethylamine borane, which was then in 10 mole percent excess. This solution was added under argon to 240 ml of Laurelsene (ARCO Chemical) at 190°C with stirring over a period of 20-30 minutes. Laurelsene is the trade name of a purified kerosene which is essentially free of olefins and aromatic compounds. As the drops of solution hit the heated kerosene, reaction occurred yielding the bistriethylammonium salt of $\text{B}_{12}\text{H}_{12}^{2-}$ and hydrogen. The mixture was stirred at 190°C for another 5-10 minutes then cooled to 50-60°C. The solid was filtered and washed free of kerosene with diethyl ether. The crude product typically weighed about 77 g, or 90% yield based on decaborane.⁽¹¹⁾

This material was dissolved in an excess of cold aqueous sodium hydroxide and filtered to remove insoluble by-products. The triethylamine was then removed by extraction with toluene and the mixture acidified with acetic acid, diluted and chlorinated as described previously at atmospheric pressure, 90°C.⁽⁷⁾ Extraction and crystallization of $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$ were carried out as previously described. Following the second crystallization from tetrahydrofuran-water, the salt was heated in vacuo on the glass vacuum line to 150-200°C.

2.2 PURIFICATION OF SOCl_2 AND ELECTROLYTES AND CELLS FOR PULSE POLARIZATION ANALYSIS

The preparation of electrolyte and test cells has been described previously.⁽⁷⁾ The volume of electrolyte in each of the test cells was measured directly upon completion of the pulse polarization measurements. The mathematical treatment of the data obtained during these measurements was also described previously.

3. RESULTS AND DISCUSSION

3.1 PREPARATION OF $B_{12}H_{12}^{2-}$ AND AQUEOUS CHLORINATION OF $B_{10}H_{10}^{2-}$ AND $B_{12}H_{12}^{2-}$

The most important reason for changing the procedure for the synthesis of $B_{12}H_{12}^{2-}$ was that the yield based on decaborane may be substantially increased. By reacting decaborane with sodium borohydride in diethylene glycol dimethyl ether, the yield is typically 60%.⁽¹²⁾ Reaction of decaborane in purified kerosene with triethylamine borane⁽¹¹⁾ raises the yield to about 90%. The reaction must still be carried out in the absence of oxygen. The kerosene must be free of all aromatics and olefins to prevent reduction of the unsaturated sites, formation of byproducts and loss of starting material.

Prior to the chlorination of $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ in aqueous solution, triethylamine present as the cation $N+(C_2H_5)_3H$ must be removed. Triethylammonium salts of partially chlorinated $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$, or $B_{12}H_{12}^{2-}$ itself, are all difficultly soluble in water and therefore interfere with the complete chlorination of the anions. Chlorination proceeds to completion much more quickly in a homogeneous liquid mixture. Presence of ammonia or substituted amines in the solution could also react with chlorine yielding explosive chloramines.⁽¹³⁾

Although initial reaction proceeds rapidly and should be moderated in a water-ice bath, complete chlorination of $B_{12}H_{12}^{2-}$ in water at atmospheric pressure near 100°C takes several days. The progress of the reaction must be checked periodically to be certain that no hydride groups remain. Infrared analysis of the dried nickel ammine derivative described in the previous report,⁽⁷⁾ prepared from small aliquots taken from the reaction flask, is a convenient and effective means of determining when complete chlorination has occurred. The anion is stable under the conditions of the chlorination reaction and is not destroyed by prolonged contact with excess chlorine.

3.2 PURIFICATION OF $Li_2B_{10}Cl_{10}$ AND $Li_2B_{12}Cl_{12}$ BY CRYSTALLIZATION

Crystallization of $Li_2B_{12}Cl_{12}$ and $Li_2B_{12}Cl_{12}$, formed by reaction of the triethylammonium salts with excess lithium hydroxide, is necessary to purify the salts. The crystallization was carried out in a mixture of dry tetrahydrofuran with a small amount of water. The salts are insoluble in the dry ether, but are highly soluble if the solvent is slightly wet. The water-tetrahydrofuran azeotrope contains only 5% water and boils at 64°, just two degrees below the boiling point of the dry ether.⁽¹⁴⁾ It is

therefore necessary to start with a solution which contains as little water as possible, use a good column, and distill slowly. The etherial solution may be dried sufficiently by equilibration with solid lithium chloride, as described previously.⁽¹⁵⁾ If instead fresh dry ether is added in large amounts, the stabilizer used to prevent autoxidation of the solvent is concentrated in the solution. The distillate used for the second crystallization is not employed merely to save ether. The distillate is also free of stabilizer. Addition of a small amount of water to the distillate may be necessary to dissolve all of the crystallized salt. At least two crystallizations are required to remove free lithium chloride from either salt. Recrystallized $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ may be checked for free chloride using aqueous silver nitrate since $\text{Ag}_2\text{B}_{10}\text{Cl}_{10}$ is highly soluble and stable in water. For $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$, the test may be carried out in acetonitrile.

3.3 THERMAL STABILITY OF $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ AND $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$

Both $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ were found to have limited thermal stability. A sample of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ when heated to 200°C in vacuum discolored slightly but noticeably. When heated to 300°C overnight it discolored extensively. When a sample of this material was taken for testing not all of it dissolved in water, some of it reacted with water, and free chloride was detected when silver nitrate was added to the acidified solution. This shows that the $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ was at least partially decomposed on heating to these temperatures. A sample of $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$ when heated to 300°C turned light gray.

The thermal stability of other $\text{B}_{10}\text{Cl}_{10}^{2-}$ derivatives has been previously discussed.⁽¹⁰⁾ $\text{Cs}_2\text{B}_{10}\text{Cl}_{10}$ suffered only a 4% weight loss when heated in vacuo to 600°C. In contrast, $\text{H}_2\text{B}_{10}\text{Cl}_{10} \cdot 4\text{H}_2\text{O}$ decomposed completely when heated to 260°C in vacuo for 5 hours.⁽¹⁶⁾ We assumed that $\text{B}_{10}\text{Cl}_{10}^{2-}$ was unstable in the latter case because of reactions involving aqueous acid. This assumption appears to be oversimplified.

Our results suggest that the size of the cation affects the stability of the anion. The larger the cation, the more stable is the anion. Cation size has been observed to affect the stability of BX_4^- salts where X is a halogen. BCl_4^- salts, for example, are less stable with small cations.^(17,18) On the basis of X-ray structures for $\text{B}_{10}\text{H}_{10}^{2-}$ ⁽¹⁹⁾ and $\text{B}_{12}\text{H}_{12}^{2-}$ ⁽²⁰⁾ and covalent and van der Waals radii,⁽²¹⁾ the chlorine atoms in both $\text{B}_{10}\text{Cl}_{10}^{2-}$ and $\text{B}_{12}\text{Cl}_{12}^{2-}$ are almost touching. Polarizing cations such as lithium are apparently able at high temperature to abstract chloride from the anionic moiety.

The thermal stability of these anions therefore appears to be affected by two parameters. One is the chloride-chloride repulsion, a steric effect, which can lower the strength of the molecular bonding. The other is the ability of a cation with high charge density, such as Li^+ , to polarize the anion and in this case remove the chloride to form LiCl which has a much higher lattice stabilization energy than the lithium salt of the polyhedral borate.

It has been necessary to heat these salts for prolonged periods of time at reduced pressure in order to remove solvents from the final recrystallization in the purification after the synthesis. If the temperature is increased to reduce the time required, partial or total decomposition of the salts is now known to result. We will continue to work on this problem. Other than this, the currently used syntheses appear to be the best laboratory preparation we can devise at this time.

3.4 EFFECT OF TEMPERATURE ON THE MEASURED PROPERTIES OF THE CHEMICALLY PASSIVATING FILM ON LITHIUM IN SOCl_2 WITH TETRACHLORALUMINATE

It has been reported that the voltage delay is affected by the temperature at which complete cells are stored.⁽²²⁾ However, the thickness and resistance of the film measured by capacitance and micropolarization measurements (the "inner" film) was found not to be affected by temperature.⁽⁷⁾ Therefore, we examined the properties of the inner film as a function of temperature. All previous measurements had been carried out at room temperature.⁽⁷⁾

After storage for three months at 55°C , two glass cells containing lithium working, reference, and counter electrodes were measured by pulse polarization techniques to determine the minimum film thickness and reaction resistance of the inner film on each working electrode before and after cooling to room temperature. The results are shown in Table 1.

Table 1. Solid Electrolyte Interphase Thickness and Resistivity at 28°C and 55°C

Cell #	Parameter	28°C	55°C
42C	d_{min}	$4.5 \times 10^3 \text{ \AA}$	$3.3 \times 10^3 \text{ \AA}$
	R_r	25 K Ω	10.7 K Ω
	specific resistivity	$5.5 \times 10^8 \text{ ohm cm}$	$3.3 \times 10^8 \text{ ohm cm}$
42D	d_{min}	$5.8 \times 10^3 \text{ \AA}$	$5.5 \times 10^3 \text{ \AA}$
	R_r	38.6 K Ω	23.6 K Ω
	specific resistivity	$6.7 \times 10^8 \text{ ohm cm}$	$4.2 \times 10^8 \text{ ohm cm}$

The measurements show that the measured LiCl layer was more conductive at 55°C than at 28°C, and that the film thickness was not strongly affected by the higher temperature. The specific resistivity was significantly lower at the higher temperature which might reflect the higher conductivity known to occur in solid salts at higher temperature. For these calculations, the dielectric constant of solid LiCl was assumed to be the same at both temperatures. The inner layer evidently regulates the growth of the outer layer without itself undergoing significant net change in its average thickness. Lithium chloride present in the outer layer should involve transport in some way through the inner layer, since the salt must form by concurrent oxidation of the metal and reduction of the solvent. The inner layer may undergo a continuous process of breaking up, releasing material to the outer layer and then reforming by further corrosion of the metal during reaction directly with the solvent. The increase in the thickness of the outer layer then would cause the observed enhancement of the delay problem.

3.5 EFFECT OF THE LITHIUM AREA TO ELECTROLYTE VOLUME RATIO OR THE PROPERTIES OF LiCl FILMS ON LITHIUM IN SOCl_2 WITH TETRACHLORALUMINATE

The quotient A/V , or the ratio of the area of exposed lithium to the volume of solvent or electrolyte, has been observed to influence gassing rates in corrosion tests using organic solvents.^(8,9) These authors observed that the greater the A/V ratio, the greater the amount of gassing.⁽⁹⁾ This result was unexpected. In the previous report d_{\min} , the inner film thickness, and R_r , the inner film resistance for lithium electrodes in $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte were plotted against time.⁽²³⁾ In both plots it is quite noticeable that the cell E is out of line. It was known at that time that the area of the electrodes in cell E was noticeably less while the volume of electrolyte was approximately the same.

Based on our previous experience and on the published work we measured the volume and calculated A/V ratios in all of our test cells. The variation in the A/V ratios was such that any effect on film growth rate was lost in experimental scatter except for the two cells stored at 72°C. The A/V ratios for these cells are compared to the previously reported⁽⁷⁾ values of d_{\min} in Table 2. When A/V was greater the film was significantly thicker.

The results shown in Table 2 and in the previously published work^(8,9) can be explained if soluble products resulting from corrosion catalyze further film building or gassing reactions (autocatalysis). For a given rate of reaction of the solvent or electrolyte with a unit area of lithium,

Table 2. Comparison of the A/V Ratios
with the Values of d_{\min}

Cell #	A/V	d_{\min} after storage at 72°C			
		1 day	3 days	10 days	31 days
42E	0.138 cm^{-1}	$.35 \times 10^3 \text{ Å}$.81	1.3	3.6
42F	0.96	1.5	2.4	2.4	4.1

the concentration of soluble products resulting from lithium corrosion and film formation would be higher if the ratio of surface area to liquid volume were higher. The higher concentration of these products would then cause faster film growth.

An analogous effect has been observed for voltage delay in different types of cells. These data are presented in Table 3.

Table 3. Voltage Delay in AA Bobbin Cells
Compared with Normal D Cells

Cell Type	Current Density	Time to Min. Potential	Min. Potent.	Time to 3 Volts	Volts at 30 Sec	Storage Time
AA bobbin (a)	$.75 \text{ mA/cm}^2$	1 sec.	2.97 V	.35 sec.	3.25	38 days
Wound D (b)	1 mA/cm^2	1 sec.	2.5 V	3 sec.	3.1	20 days
(a) average of 4 cells, a 5th cell did not delay. (b) from Figure 5 reference 22.						

The A/V ratio in wound "D" cells is greater than the A/V ratio in double A cells. The greater delay observed in the wound D cells would suggest that autocatalysis also affects formation of the outer film.

BIBLIOGRAPHY

- 1) N. Marincic, and A. Lombardi, ECOM 74-0108-F; April 1977.
- 2) A.N. Dey and C.R. Schlaikjer, Proc. Power Sources Symposium 26, 47 (1974).
- 3) E. Peled, Abstract 4, Electrochemical Society Fall Meeting, Atlanta, October 1977.
- 4) E. Peled, C.R. Schlaikjer, and N. Marincic; Abstract 553 Electrochem. Society Spring Meeting, Seattle, Wash., May 1978.
- 5) E. Peled, and H. Straze, J. Electrochem. Soc. 124, 1030 (1977).
- 6) Y. Avigal and E. Peled, J. Electroanalytical Chem. 76, 135 (1977).
- 7) Report #78-0558-1, March 1979, for this present contract.
- 8) F.W. Dampier and P.E. Krouse, Abstract #23, Electrochem. Soc. Fall Meeting, October 1974.
- 9) J.D. Doe, F.W. Dampier, K. Jeffries, P.E. Krouse, N. Margalit, E.J. Merrick, L.C. Thompson, Jr., Final Report AFAPL-TR-74-63 December 1974, Contract No. F33615-72-C1470, ESB Inc.
- 10) W.H. Knoth, H.C. Miller, J.C. Sauer, J.H. Balthis, Y.T. Chia, and E.L. Muettertities, Inorg. Chem. 3, 159 (1964).
- 11) H.C. Miller, and E.L. Muettertities, Inorganic Syntheses, 10, 81 (1967).
- 12) R.N. Adams, A.R. Siedle, J. Grant, Inorg. Chem. 3, 461, (1964).
- 13) C.R. Schlaikjer; 28th Power Sources Symposium, Atlantic City, New Jersey, June 1978.
- 14) L.H. Horsley, editor, "Azeotropic Data-III" Amer. Chem. Soc., Wash., D.C. (1973) p. 21.
- 15) C.R. Schlaikjer, U.S. Patent 4,020,240.
- 16) J.A. Forstner, T.E. Haas, and E.L. Muettertities; Inorg. Chem. 3, 155 (1964).
- 17) E.L. Muettertities, J. Am. Chem. Soc. 79, 6563 (1957).
- 18) F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry" 3rd edition. Wiley-Interscience, New York 1972, p. 236.
- 19) R.D. Dobrott and W.N. Lipscomb; J. Chem. Phys 37, 1779 (1962).
- 20) J.A. Wunderlich and W.N. Lipscomb; J. Am. Chem. Soc. 82, 4427 (1960).
- 21) Ref. 18, pp. 117-120.
- 22) N. Marincic, A. Lombardi, and C.R. Schlaikjer; Proc. of Power Sources Symposium 27, 37 (1976).
- 23) Ref. 7, Figures 5 and 6.

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